TITLE: METHOD FOR IMPROVING THE PERFORMANCE OF ENGINES POWERED BY LIQUID HYDROCARBON FUEL

Cross-reference to Related Applications

[0001] The present application is a continuation-in-part of U.S. Patent Application Serial No. 10/453,803, incorporated herein by reference. The present application also is related to U.S. Patent No. 6,599,337, incorporated herein by reference.

Field of the Invention

[0002] The application relates to a method for improving the performance of engines powered by liquid hydrocarbon fuel.

Background

[0003] Materials often are added to flowing fluids in order to reduce the energy lost due to friction, or drag, thus permitting the movement of more fluid at the same differential pressure. Materials for reducing drag in flowing fluids generally are known by the generic names "flow improver" or "drag reducer additive" (sometimes referred to as "DRA").

[0004] Unfortunately, the DRA in liquid hydrocarbon fuels has the potential to cause a number of problems. Methods are needed to improve the performance of engines that use liquid hydrocarbon fuel otherwise contaminated with DRA.

Summary

[0005] The present application provides a method for improving performance of an engine. The method comprises contacting contaminated liquid hydrocarbon fuel comprising an initial concentration of DRA with one or more effective DRA removal agent under conditions effective to produce decontaminated liquid hydrocarbon fuel

comprising a reduced concentration of said DRA, and feeding said decontaminated liquid hydrocarbon fuel to said engine.

Detailed Description

[0006] The presence of DRA in motor gasoline, even in sheared form, has caused increased intake valve deposits, plugging of fuel filters, and increased combustion chamber deposits. In jet engines, use of aviation jet fuel containing even sheared DRA has been shown to adversely affect the ability of the jet engines to reignite if a flameout occurs. In diesel fuels, DRA may cause plugging of fuel filters and strainers and/or increased fuel injector deposits. DRA is prohibited in aviation turbine fuels, although DRA has been observed as a contaminant due to accidental addition or other non-intentional means. The presence of DRA in aviation turbine fuel may result in downgrading of the entire batch to non-aviation kerosene or diesel fuel, both of which generally have less market value.

[0007] The present application provides methods for improving engine performance by contacting contaminated liquid hydrocarbon fuel comprising DRA under conditions effective to produce decontaminated liquid hydrocarbon fuel comprising a reduced concentration of DRA, and feeding the decontaminated liquid hydrocarbon fuel to the target engine. The use of the decontaminated liquid hydrocarbon fuel avoids downgrading of aviation fuels and, in other motor fuels, decreases plugging of fuel filters, and formation of deposits on intake valves, combustion chambers, fuel injectors, and will improve the reignition properties of the aviation jet fuel.

"Liquid Hydrocarbon Fuel"

[0008] By "liquid hydrocarbon fuel" is meant any hydrocarbon that is liquid under conditions of transport and/or storage. Suitable liquid hydrocarbon fuels include, but are not necessarily limited to those having a boiling range of from about 150 °F to about 750 °F, which may be used as a fuel. In one embodiment, the liquid hydrocarbon fuel is selected from the group consisting of liquefied natural gas (LNG), liquefied petroleum gas (LPG), motor gasoline, aviation gasoline, distillate fuels such as diesel fuel and home heating oil, kerosene, jet fuel, No. 2 oil, residual fuel, No. 6 fuel, or bunker fuel. In a preferred embodiment, the liquid hydrocarbon fuel is selected from the group consisting of diesel fuel, jet fuel, aviation gasoline, and motor gasoline. In a more preferred embodiment, the liquid hydrocarbon fuel is jet fuel, at least in part due to the stringent requirements applicable to jet fuel and DRA. The phrase "jet fuel" refers to both commercial jet fuel (Jet A, Jet A-1, and JET B) and military jet fuel, such as JP-4, JP-5, JP-8 and the like.

"DRA"

[0009] The term "drag reducer additive" or "DRA" refers to any material which is added to a liquid hydrocarbon fuel to reduce fluid flow drag. DRA's include, but are not necessarily limited to polyolefin polymers and DRA's comprising polar groups.

[0010] In a preferred embodiment, the DRA includes, but is not necessarily limited to, non-polar long-chain polyolefin polymers, generally referred to as "polyalphaolefins," having a "peak" molecular weight sufficiently high to allow the polymers to reduce fluid flow drag. Suitable polyalphaolefins are believed to have a peak molecular weight of about 1 million Daltons or more, more preferably about 10 million Daltons or more, most preferably about 25 million Daltons or more. The

"peak" molecular weight refers to the peak that typically is measured as the drag reducer is eluted and detected during gel permeation chromatography.

[0011] Suitable polyalphaolefins comprise polymerized linear alpha olefin (LAO) monomers having from about 2 to about 40 carbon atoms, preferably from about 2 to about 30 carbon atoms, more preferably from about 4 to about 20 carbon atoms, most preferably from about 6 to about 12 carbon atoms. An especially preferred embodiment for a DRA which is effectively removable by the activated carbons and/or graphites described herein comprises at least two different LAO's, preferably having from about 6 to about 12 carbon atoms, the number of carbon atoms of the "at least two different LAO's" differing by 6.

[0012] Polyalphaolefins having relatively high molecular weights are required to impart good drag reduction. Suitable polyalphaolefins "are made by a variety of processes, including but not necessarily limited to solution polymerization and bulk polymerization. Bulk polymerization is said to produce "ultra-high molecular weight polyolefin drag reducers [that] are significantly larger (molecular weight basis) than the best molecular weights made by solution polymerization." See U.S. Patent No. 5,504,132. Preferred DRA's for removal according to the process described herein are made by solution polymerization.

[0013] Without limiting the invention to a specific theory or mechanism of action, the very large polyalphaolefins made by bulk polymerization may be more difficult to adsorb onto and retain on carbonaceous removal agents. In contrast, the polyalphaolefins made by solution polymerization may be more readily adsorbable onto the removal agents, and more readily retained by the removal agents.

[0014] In another embodiment, the DRA comprises polar groups. Examples of suitable polar groups include, but are not necessarily limited to organic polar groups. Organic polar groups generally comprise a moiety selected from the group consisting of oxygen, sulfur, nitrogen, halogen, phosphorus, unsaturated carbon-carbon bonds, and combinations thereof.

[0015] The DRA may comprise other components besides the polyolefin moieties. Examples of such components include, but are not necessarily limited to surfactant, catalyst residue, other additives, and other byproducts from the production of the polymer. The polymer itself may contain other non-olefin monomer units as well.

[0016] DRA's generally are unsheared, partially sheared, or fully sheared. An additive that is fully sheared is one that is degraded in molecular weight to the maximum extent possible using high shear devices such as pumps, static mixers, etc. Commercially available DRA's include, but are not necessarily limited to, CDR ® Flow Improver, REFINED POWER ™, and REFINED POWER II™, manufactured by ConocoPhillips; EN-660 Flow Improver, manufactured by Energy 2000 LLC; and FLO®XS and FLO®XL, manufactured by Baker Petrolite. In a preferred embodiment, the DRA is FLO®XS and equivalents thereof.

[0017] As liquids containing DRA travel through pumps, pipelines and other equipment, the DRA typically degrades through shearing action, resulting in a reduction in the molecular weight of the DRA. The degraded DRA generally is sheared or partially sheared DRA. Upon reaching the ultimate destination, the contaminated liquid hydrocarbon fuel may contain a significant amount of DRA, including that in the sheared and partially sheared form. This DRA is sometimes referred to herein and in the claims as the "initial concentration of DRA."

Removal Agents

[0018] According to the present application, the contaminated liquid hydrocarbon fuel comprising an initial concentration of DRA is contacted with one or more effective removal agents under conditions effective to produce "decontaminated liquid hydrocarbon fuel" comprising a reduced amount of DRA. The decontaminated liquid hydrocarbon fuel is fed to the engine.

[0019] Suitable removal agents are effective to achieve a % DRA removal of about 10% or more when 1 g of the removal agent is added (in increments with agitation) to 100 ml. of contaminated liquid hydrocarbon fuel comprising from about 8 to about 12 ppm of unsheared target DRA. Preferred removal agents achieve a % DRA removal of about 20% or more, preferably 30% or more; more preferably about 40% or more under the same conditions.

[0020] Examples of suitable removal agents include, but are not necessarily limited to graphites, activated carbons, and fresh attapulgus clay.

-Graphites

[0021] Preferred DRA removal agents are graphites. Graphite is a crystalline form of carbon found as a naturally occurring mineral in many locations around the world. Graphite can be amorphous ("amorphous graphite"). Graphite also can have a perfect basal cleavage which, coupled with its extreme softness, gives it an oily, slippery feel. Suitable graphites include, but are not necessarily limited to natural graphites, synthetic graphites, and expanded graphites. Each of these graphites is commercially available in various forms, including, crystalline lumps, crystalline large flakes, crystalline medium flakes, crystalline small flakes, and powder form. Artificial graphite can be manufactured from petroleum coke and is primarily used to

make electrodes. The virgin by-product of such electrode production has a carbon content as high as 99.9%, and can be a relatively inexpensive source of graphite agent, to highly refined natural graphite. Suitable candidate graphites are commercially available, for example, from Asbury Carbons, Inc., Asbury, NJ; Superior Graphite Co., Chicago, IL; Stanford Materials Corporation, Aliso Viejo, CA; and others.

[0022] Preferred graphites are selected from the group consisting of graphite powders and graphite particulates. The graphite particulates preferably are granular and have an average diameter of from about 0.01 microns to about 10,000 microns; preferably from about 0.1 microns to about 1,000 microns; most preferably about 1 micron to about 100 microns. Preferred graphites have a porosity sufficient to provide an adsorption capacity of about 0.01 wt.% or more, preferably about 0.03 wt.% or more, most preferably about 0.04 wt% or more, when exposed to a preferred DRA. Suitable and preferred graphites are commercially available from Superior Graphite Company. Preferred graphite products comprise, but are not necessarily limited to, purified carbon, natural graphite, silica (crystalline quartz), and synthetic graphite.

[0023] Graphites that demonstrated commercial viability for adsorbing unsheared and sheared BAKER PETROLITE FLO® XS and equivalents included GRAPHITE 2126, GRAPHITE 2139, GRAPHITE 3726, GRAPHITE 3739, GRAPHITE 5526, GRAPHITE 5539, GRAPHITE 9026, GRAPHITE 9039, and GRAPHITE GA-17, available from Superior Graphite Co. The foregoing graphites exhibited an adsorption capacity for unsheared and sheared BAKER PETROLITE FLO® XS of about 0.01 wt% or more.

[0024] Preferred commercially available graphites for adsorbing unsheared BAKER PETROLITE FLO® XS and equivalents included GRAPHITE 2126, GRAPHITE 2139, GRAPHITE 3726, GRAPHITE 3739, GRAPHITE 5539, GRAPHITE 9039, and GRAPHITE GA-17. The foregoing graphites exhibited an adsorption capacity for unsheared BAKER PETROLITE FLO® XS of about 0.02 wt% or more. Preferred commercially available graphites for adsorbing sheared BAKER PETROLITE FLO® XS and equivalents included GRAPHITE 2126, GRAPHITE 2139, GRAPHITE 3726, GRAPHITE 3739, GRAPHITE 9026, and GRAPHITE 9039. The foregoing graphites exhibited an adsorption capacity for sheared BAKER PETROLITE FLO® XS of about 0.018 wt% or more.

[0025] Even more preferred commercially available graphites for adsorbing unsheared BAKER PETROLITE FLO® XS and equivalents included GRAPHITE 2139, GRAPHITE 3726, GRAPHITE 3739, GRAPHITE 5539, GRAPHITE 9039, and GRAPHITE GA-17. The foregoing graphites exhibited an adsorption capacity for unsheared BAKER PETROLITE FLO® XS of about 0.03 wt% or more.

[0026] Most preferred graphites, particularly for adsorbing unsheared BAKER PETROLITE FLO® XS and equivalents thereof, include but are not necessarily limited to GRAPHITE 2139 and GRAPHITE 3739. The foregoing graphites exhibited an adsorption capacity for unsheared BAKER PETROLITE FLO® XS of about 0.04 wt% or more. Most preferred graphites, particularly for adsorbing sheared BAKER PETROLITE FLO® XS and equivalents thereof, include but are not necessarily limited to GRAPHITE 3726 and GRAPHITE 3739. The foregoing graphites exhibited an adsorption capacity for sheared BAKER PETROLITE FLO® XS of about 0.025 wt% or more.

-Activated carbons

[0027] Suitable activated carbons for use as effective removal agents are identified in U.S. Patent No. 6,599,337, which has been incorporated herein by reference. Suitable activated carbons are commercially available, for example, from Allchem Industries, Inc., Beta Chemicals, Calgon, Coyne Chemical Co., Elf Atochem North America, Inc. (Performance Products), R. W. Greef & Co, Inc., Kingshine Chemical Co., Ltd., Mays Chemical Co., Inc., Mitsubishi International Corp. (Industrial Specialty Chemicals Div.), Spectrum Chemical Mfg. Corp., Norit Americas, Inc. and others.

[0028] Commercially viable activated carbons, which have been demonstrated to be suitable to remove Baker Petrolite FLO® XS and equivalents thereof include, but are not necessarily limited to, CALGON ADP, CALGON COLORSORB, CALGON WPX, NORIT A SUPRA, NORIT CA 1, NORIT FGD, NORIT HDB, SXO POWDER, and CARBON 5565. Preferred activated carbons demonstrated to be useful for removing Baker Petrolite FLO® XS and equivalents thereof include, but are not necessarily limited to CALGON WPX, NORIT A SUPRA, NORIT CA1, NORIT FGD, NORIT HDB, SXO POWDER and CARBON 5565. Most preferred activated carbons demonstrated to be useful for removing Baker Petrolite FLO® XS and equivalents thereof include, but are not necessarily limited to NORIT A SUPRA, NORIT CA1, NORIT FGD, and NORIT HDB.

-Fresh Attapulgus Clay

[0029] Also suitable for use as a removal agent is fresh attapulgus clay. "Fresh" attapulgus clay is effective to remove about 10% or more of a target DRA when 1 g of the attapulgus clay is added in increments of from about 0.02 gram to about 0.1 gram,

with agitation, to 100 ml. of contaminated liquid hydrocarbon fuel comprising from about 8 to about 12 ppm of the unsheared target DRA.

[0030] Attapulgus clay generally comprises granules comprising a conglomerate of fundamental particles. A majority of the granules typically have a mesh size of from about 30 to about 90.

Removal of DRA From Liquid Hydrocarbon Fuels

[0031] The contaminated liquid hydrocarbon DRA is contacted with the DRA removal agent(s) using any suitable method. A preferred method for use, particularly with relatively viscous fuel, comprises incremental addition of the DRA and agitation of the resulting mixture. Due to the difficulty in providing for incremental addition and agitation in most commercial situations, it may be preferred to simply pass the contaminated liquid hydrocarbon fuel through a bed comprising one or more effective removal agent(s) until the bed DRA removal rate is so low that the bed must be regenerated or replaced.

[0032] In a preferred embodiment, the removal agent is incorporated into a system for filtering the contaminated liquid hydrocarbon fuel to remove the DRA. The construction and type of filter will vary depending upon the liquid hydrocarbon fuel to be treated and the location of treatment.

[0033] Suitable locations for the filter system comprising the DRA removal agent include, but are not necessarily limited to: at a refinery; between a refinery and a fuel terminal; at a fuel terminal; between two different fuel terminals; between a fuel terminal and an airport storage tank; at an airport storage tank; between a fuel terminal and a tanker truck; at a tanker truck; between an airport storage tank and a tanker truck; between two different tanker trucks; between a tanker truck and an

engine, at a fuel dispenser (such as a gasoline pump); between a fuel dispenser and a vehicle comprising the engine; and, at the engine.

[0034] The removal agent may or may not be preheated prior to use to a temperature effective to remove any adsorbed water without damaging the removal agent(s).

Fuel Delivery to Engine

[0035] Once the liquid hydrocarbon fuel is treated with the effective removal agent under conditions effective to produce decontaminated liquid hydrocarbon fuel, the decontaminated liquid hydrocarbon fuel is fed to the target engine using known methods and devices.

[0036] Persons of ordinary skill in the art will recognize that many modifications may be made to the foregoing without departing from the spirit and scope thereof. The embodiment described herein is meant to be illustrative only and should not be taken as limiting the invention, which is defined in the following claims.